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Treatment of dinitrotoluene in an aqueous environment by electro-peroxidisulfate process using a central composite design

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ABSTRACT

In this study, through electro-peroxydisulfate (E-PDS), the removal of dinitrotoluene (DNT) in synthetic wastewater was explored. The influence of crucial parameters, including applied current, the ratio of peroxydisulfate to DNT, pH, and also the treatment time on the DNT removal was investigated. For statistical analysis and experimental design, a central composite design was applied. The quadratic model had high correlation coefficients ($R^2 = 0.999$ and R^2 adjusted = 0.998). Based on experimental results, it was detected that the treatment time and the ratio of peroxydisulfate (PDS) to DNT had more influence on DNT removal. The neutral pH was observed as the optimum point. Graph of Pareto analysis offered significant information for the impact of variables on the response. The optimal condition was achieved as pH at 6.5, $S_2O_8^{-2}$/DNT = 1.6, applied current at 2.4 A, and 40 min of reaction time. At achieved optimum conditions, about 90.9% and 67% of DNT and chemical oxygen demand (COD) were removed, respectively, and the amounts of COD were decreased from 350 to 100 mg L^{-1}. In the attained optimum conditions, the electrical energy consumption (EEC) and cost evaluation for E-PDS were achieved at 4.5 kWh kg^{-1} COD removed and 0.37 USD kg^{-1} COD removed, respectively.

Keywords: Sulfate radical; Electro-peroxydisulfate; Advanced oxidation processes; Dinitrotoluene (DNT)

1. Introduction

Several chemical industries and domestic wastewaters have substantial volumes of organic pollutants, potentially posing significant hazards to the environment and human beings. As a result, during the wastewater remediation process, efficient removal of organic pollutants in an aqueous environment is a significant concern which results in a growing requirement for the advent of highly sophisticated wastewater treatment techniques [1–3].

Dinitrotoluene is an imperative petrochemical compound primarily used to produce toluene diisocyanate, an important intermediate for the production of polyurethane. Also, dinitrotoluene (DNT) derivatives are essential precursors for manufacturing paints, dyes, explosives, and rubber. Based on the high poisonousness and probable carcinogenicity, the wastewater polluted with DNTs and their relative derivatives should be disposed carefully before being released into the environment [4].

Until now, several methods have been used for the mineralization of DNT in wastewater owing to their resistance vs. biological approaches [5].

Advanced oxidation processes (AOPs) show much promise for remediation of refractory organic pollutants properly in wastewaters. The recalcitrant target constituents must be changed into their highest stable oxidation state throughout the oxidation, including H_2O, CO_2, oxidized mineral anions, and easily degradable molecules, which are

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possibly bio-degradable. Operational conditions, pollutant category, and process limitations are the main parameters that must be regarded when choosing the best oxidation process to degrade target constituents [6,7].

Recently, the sulfate radical ($SO_4^{\bullet-}$) interests growing consideration due to its more oxidizing ability, wider pH extent, and extensive lifetime [8,9]. Electro-oxidation (EO) can degrade organic contaminants via direct and indirect oxidation as one of the modest and operative AOPs, under exterior electrical fields [10]. The pollutants are oxidized by the produced hydroxyl radicals on the anode surface through direct oxidation [11,12]. Indirect oxidation is proficient through the addition of different metal ions (Fe, Mn, Ce, etc.) for transmission of electrons and oxidizing pollutants in solution [13]. But, the capability of the conventional EO method can be restricted by the mass transfer and limited size of the anode.

Recently some investigators described that the peroxydisulfate (PDS) could be activated by the EO process to produce sulfate radicals [14]. Despite other activation methods such as ultrasonic, ultraviolet, transition metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}) and heat [15,16], the EO purpose is not only a single activation technique but also cooperates with PDS to increase EO redox reactions [17], then accelerating the production of hydroxyl radicals and subsequent degradation of pollutants. Additionally, the PDS could be considered an electrolyte and electron transporter, which could progress current density and increase the electron and mass transfers.

Peroxydisulfate has a special structure that enables it to degrade to reactive species simply by additional activation methods. The mentioned methods include activation through metal and metal oxide catalysts, ultra-violet radiation, transition metals, base, and heat. Since the activation by metals has advantages like the possibility of catalyst reuse and less required power, they are the focus of attention [18,19].

In electrochemical methods, indirect oxidation and direct oxidation happen due to oxidants produced in electrochemical methods and at the surface of the anode, respectively. Through activation of peroxydisulfate by Fe^{+2} ions originating from electrolysis, the sulfate radicals were produced, and subsequently, the target pollutants were degraded [20,21].

Utilization of SO_4^{2-} as an alternative for $OH^{\bullet}$ has various advantages like higher selectivity of $SO_4^{\bullet-}$ and more extensive scope of practical pH. The redox capacities of SO_4^{2-} and $OH^{\bullet}$ are similar in the acidic environment. Nevertheless, at pH values of 7, in comparison to $OH^{\bullet}$, the $SO_4^{\bullet-}$ is a highly effective oxidant [21].

As a precursor, the utilization of peroxydisulfate for in situ formations of $SO_4^{\bullet-}$ to the decomposition of different organic contaminants in wastewater has been widely stated in various researches.

The designs of experiments are more beneficial than traditional single variable methods, since they empower the optimization and modeling of multiple factors with a powerfully summary number of trials. In addition, the central composite design (CCD), and Box–Behnken design (BBD), as RSM procedures, are the most effective to evaluate the relationship between variables and the effect of distinct variables. The BBD technique does not contain extreme combinations factor value (lowest or highest level) compared to the CCD. Thus, the CCD can accomplish runs under extreme factor value situations, certifying correct results [22–25].

Thus, this study aimed to assess the removal efficiency of DNT in electrochemical activation of PDS activated through ferrous ion with four iron electrodes. The effect of many critical parameters, including applied current, the ratio of peroxydisulfate to DNT, pH, and the treatment time, was investigated on the removal of DNT. In this way, Design–Expert (ver.12) statistical software was used.

2. Materials and methods

2.1. Materials

The used chemical reactants include potassium peroxydisulfate ($K_2S_2O_8$) and 2,4-dinitro toluene, supplied by Merck Company. Manganese dioxide, NaOH, and H_2SO_4 were provided by Sigma-Aldrich Company.

2.2. Experimental equipment and approach

As shown in Fig. 1, to conduct the experimental processes, a glass photoreactor with a volume of 1 L was utilized. A sampling connection was provided with the reactor. The reactor is made from a water jacket with an exterior flow, which is regulated by a thermostat to fix the temperature at 25°C during all tests. A Thermo bath (BW 20G made in Korean) was used to manage the temperature of the reaction mixture. A Sartorius pH meter (PT-10P instrument, made by Germany) was employed to control the initial pH of the solution. To measure the effectiveness of DNT removal, the samples were investigated through a spectrophotometer at the highest wavelength of 244 nm, and the HPLC analysis validated the outcomes. The mineralization of the mixture was considered as chemical oxygen demand (COD) removal, and it was calculated using the spectrophotometer analyzer (DR 5000, Hach, Jenway, USA) at 600 nm depending on the process guidelines stated in the prior research [26].

A schematic diagram of the used reactor in this study is shown in Fig. 1. A reactor (effective volume: 1,000 mL) was used to conduct batch experiments. Four iron electrodes (two as anode and two as cathode) with the same dimensions (200 mm × 20 mm × 2 mm) were arranged on a set of parallel plates at a distance of 2.0 cm. For each experiment, around 1 L of the artificial wastewater was studied, and for entire reactor examinations, the reaction time was controlled. The concentration of DNT was set at 100 mg L^{-1} in all runs, containing 350 mg L^{-1} of COD. The DNT removal percent was measured as the following formula [Eq. (1)]:

$$\text{Removal of DNT}\left(\%\right)=\left(\frac{\left[\text{DNT}\right]_0-\left[\text{DNT}\right]}{\left[\text{DNT}\right]_0}\right)\times 100 \quad (1)$$

where $[\text{DNT}]_0$ and [DNT] indicate the concentrations of DNT prior to and later wastewater remediation, respectively. The left-over amounts of peroxydisulfate in the wastewater samples were removed by adding a small amount of manganese dioxide powder to avoid disrupting the investigation

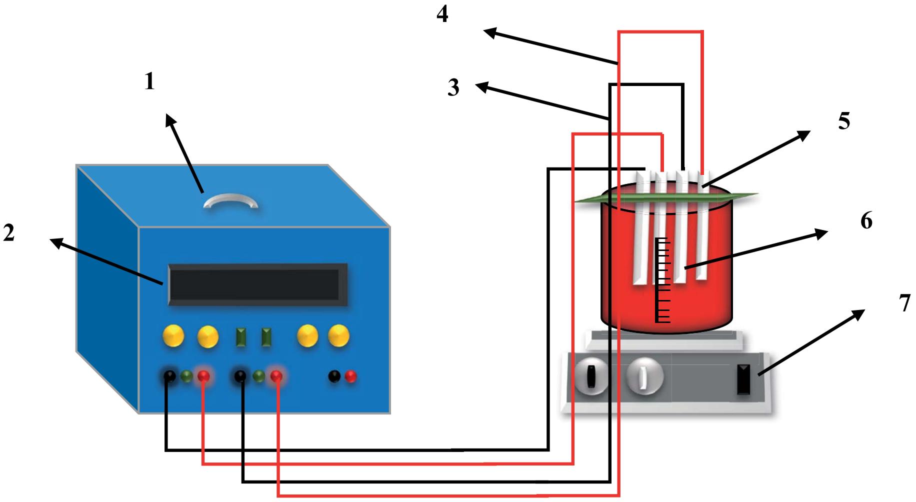

Fig. 1. Simplified demonstration of the test reactor. (1) Power supply, (2) voltage indicator and electrical current, (3) cathode connection cable, (4) anode connection, (5) Plexiglass reactor cell, (6) iron electrodes, and (7) magnetic stirrer.

of COD. The wastewater samples were filtered out to eliminate manganese dioxide particles.

2.3. Empirical setup

Table 1 demonstrates the major parameters with their levels, and the significant parameters include applied current, the ratio of peroxydisulfate to DNT, pH, and also the treatment time. Five levels were regarded for each parameter. As shown in Table 1, these levels are mathematically indicated as –2, –1, 0, +1, and +2. Design-Expert software (version 12) was employed for the experimental process and statistical exploration of results. The independent variables were selected due to preliminary experiments and previous works.

3. Results and discussion

3.1. Empirical setup and statistical examination

Besides the actual and anticipated amounts of the response, the experimental process matrix is integrated into Table 2.

Ultimate equations in terms of coded and actual factors are demonstrated as Eq. (2), respectively.

$$\begin{aligned}\text{DNT Removal}\left(\%\right) &= 75.68 + 4.61A + 1.29B - 1.37C \\ &+ 14.39D + 0.5813AB + 0.5938AC + 0.7938BD \\ &+ 0.7563CD - 1.74A^2 - B^2 - C^2 - D^2\end{aligned} \tag{2}$$

The analysis of variance (ANOVA) is shown in Table 3. The Model *F*-value of 1,399.69 suggests that the model is significant. There is only a 0.01% chance that this large *F*-value could happen because of noise [27]. The model terms are called significant, where the related possibility values (*p*-values) are less than 0.0500. The *p*-values greater than 0.1000 indicate the model factors are insignificant. In this examination, all of the model terms were significant.

Table 1
Independent variables and coded levels based on the CCD

Factor	Factor level				
	–2	–1	0	+1	+2
$S_2O_8^{2-}$ = 1.6 (*A*)	0.4	0.8	1.2	1.6	2.0
Applied current (*B*)	0. 7	1.4	2.1	2.8	3.5
pH (*C*)	3.5	5	6.5	8	9.5
Treatment time (*D*)	10	20	30	40	50

The determination coefficient (R^2) was used for controlling the prediction ability and accuracy of the models. It is being favorite to be close to 1 for displaying good prediction ability. But R^2 value cannot evaluate the model's prediction value, since the R^2 value raises as the number of terms in the model rises without seeing statistical significance [28].

Therefore, the R^2 value should be linked with the adjusted R^2 value showing the number of parameters in the test. The predicted R^2 of 0.9971 agrees with the adjusted R^2 of 0.9983.

The adjusted R^2 value reduces as the number of insignificant variables rises. An excessive variance between adjusted R^2 and R^2 values is a pointer that the model comprises insignificant terms. The variance between the actual and predicted values is being stated as residual and has an important role in the valuation of the model's capability. The adjusted R^2 value increases with an increase in the number of independent variables having an important influence on the dependent variables, and it was decreased as insignificant variables are added to the model.

The difference between R^2 and adjusted R^2 should be low for the adequacy of the model [29].

The reproducibility of the model is expressed by the coefficient of variance (CV) as the ratio between the standard error

Table 2
Different runs and mentioned results in DNT removal

Std	Run	Factor 1	Factor 2	Factor 3	Factor 4	Response 1
		A: S_2O_8/DNT	*B*: Applied current	*C*: pH	*D*: Treatment time	DNT removal (%)
1	20	0.8	1.4	5	20	46.4
2	15	1.6	1.4	5	20	53.2
3	23	0.8	2.8	5	20	46
4	27	1.6	2.8	5	20	55
5	8	0.8	1.4	8	20	40.1
6	17	1.6	1.4	8	20	50.2
7	19	0.8	2.8	8	20	40
8	30	1.6	2.8	8	20	52.5
9	14	0.8	1.4	5	40	72.2
10	26	1.6	1.4	5	40	79.5
11	13	0.8	2.8	5	40	75
12	18	1.6	2.8	5	40	84
13	3	0.8	1.4	8	40	70
14	16	1.6	1.4	8	40	78
15	6	0.8	2.8	8	40	73
16	22	1.6	2.8	8	40	84
17	11	0.4	2.1	6.5	30	59.5
18	1	2	2.1	6.5	30	78
19	7	1.2	0.7	6.5	30	60.5
20	25	1.2	3.5	6.5	30	66
21	12	1.2	2.1	3.5	30	55
22	24	1.2	2.1	9.5	30	50.3
23	9	1.2	2.1	6.5	10	37
24	21	1.2	2.1	6.5	50	93.5
25	28	1.2	2.1	6.5	30	75.5
26	2	1.2	2.1	6.5	30	76.4
27	5	1.2	2.1	6.5	30	76
28	29	1.2	2.1	6.5	30	76.5
29	4	1.2	2.1	6.5	30	74.4
30	10	1.2	2.1	6.5	30	75.3

of prediction value and the average value of the observed response. The CV below 10% implies that the model is reproducible [30].

The range in the predicted response and relevant error value of the response is presented by Adequate precision, and it is desired to have a value higher than 4 for the adequacy of the model. The CV values of the model were less than 10% (0.9718) and good precision values higher than 4 (138.19). It can be determined that the model's fitness is acceptable [31].

To determine the participation of each parameter and interactions in anticipating the response, percent contribution was measured according to Eq. (3) [31]:

$$\text{Percent contribution}\left(\%\right)=\frac{\text{SS}_F}{\text{SS}_T} \tag{3}$$

where SS_T and SS_F indicate the total sum of squares of all parameters and the sum of squares of parameters, respectively, the responses anticipated against real detected values are shown in Figs. 2–4. According to that, there is enough harmony between the anticipated values by the model and the detected values in the experiments.

The lack of fit for *F*-value at about 0.50 indicates that the lack of fit is insignificant relative to the pure error. There is an 85.21% chance that a lack of fit for this large *F*-value could happen because of noise.

3.2. 3D Plots for the removal of DNT vs. variables

The three and two-dimensional plots indicated the integrated influences of two parameters to anticipate DNT removal efficiency. The three-dimensional plots of DNT removal vs. parameters are shown in Figs. 2–4. These figures were plotted using Eq. (2). As demonstrated in the figures, raising the ratio of peroxydisulfate to DNT enhanced the DNT removal efficiency to some extent, whereas the influence of pH variation was not significant. Such results might be attributed to the high production of $SO_4^{-\bullet}$ at increased concentrations of peroxydisulfate and Fe^{2+}. The value of the $SO_4^{-\bullet}$ and the degradation of DNT in wastewater are directly proportional together and, as a result, the lowering the DNT amounts in the remediated wastewater. As suggested formerly, compared to the significant parameters, the statistical significance of the pH parameter in anticipating the response was lower [32].

3.3. Influence of the ratio of peroxydisulfate to DNT

In wastewater remediation through chemical oxidation, to decrease the chemicals cost, the concentration of chemical oxidants must be at an optimum point. To evaluate the effect of peroxydisulfate concentration, several experimental runs were conducted, and the influence of the PDS to DNT ratio was explored for different concentrations; the results are shown in Fig. 2. According to it, the influence of the PDS to DNT ratio on the decomposition of DNT was studied in the scope of 0.4 to 2, and the rising PDS to DNT ratio had a good influence on the removal of DNT till it reached the highest amounts at 1.6. Increasing the PDS to DNT ratio enhances the formation of $SO_4^{-\bullet}$ and $OH^{\bullet}$, and thus increases the degradation of DNT. Other rising in PDS to DNT ratio had no significant influence on the DNT removal effectiveness. Such a result can be explained by the scavenging influence of further PDS concentration, which has been investigated by several studies. In this situation, increasing PDS to DNT ratio scavenges $SO_4^{-\bullet}$ and $OH^{\bullet}$ and, based on the Eqs. (9) and (10) results in the generation of an ineffective oxidant like $S_2O_8^{\bullet -}$ [33]. Nevertheless, it appears that the amounts of produced total radicals were approximately fixed at PDS to DNT ratio over 1.6, and this might be related to the insignificant alternation of DNT removal at greater concentrations of PDS.

In the same way, other researchers have validated that adding extra quantities of peroxydisulfate did not additionally raise the output effectiveness.

The PDS can be activated by electrolytic through the following mechanisms [Eqs. (4)–(6)] [34]:

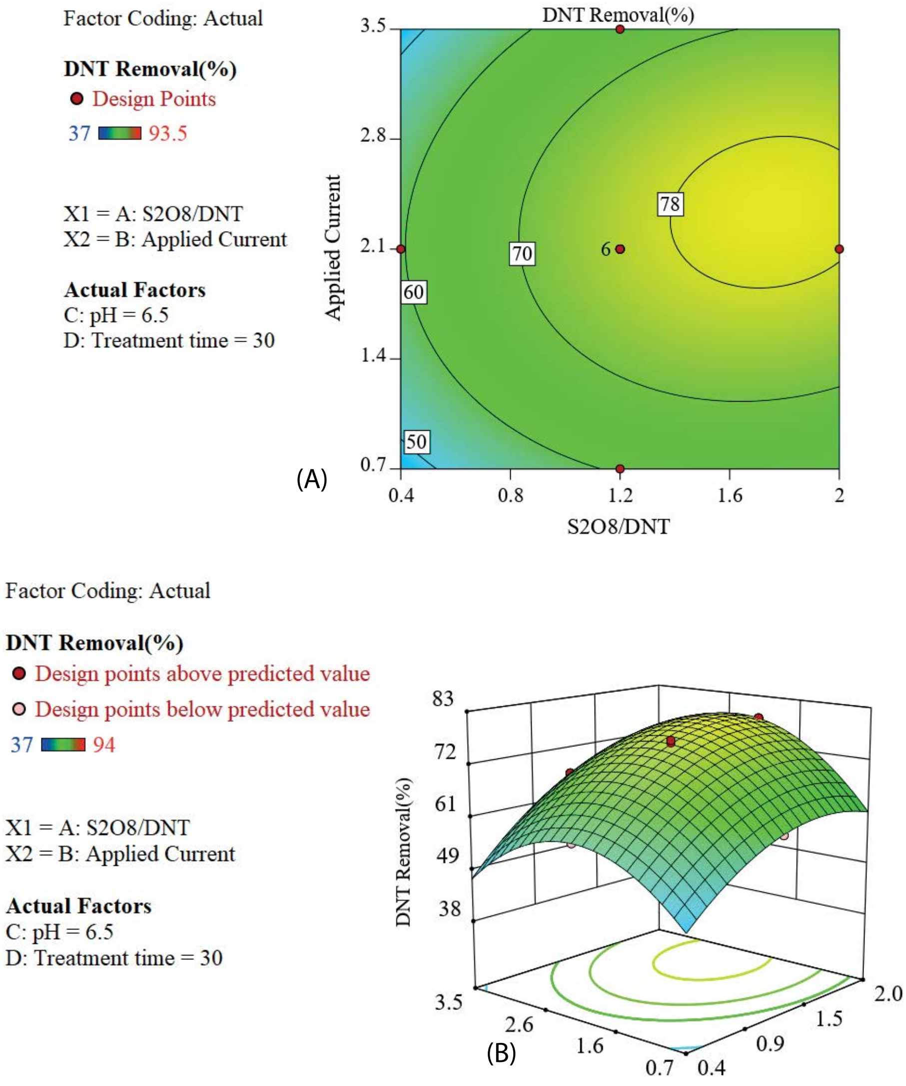

Fig. 2. (A, B) Influence of the PDS to DNT ratio on the removal of DNT at particular pH and treatment time.

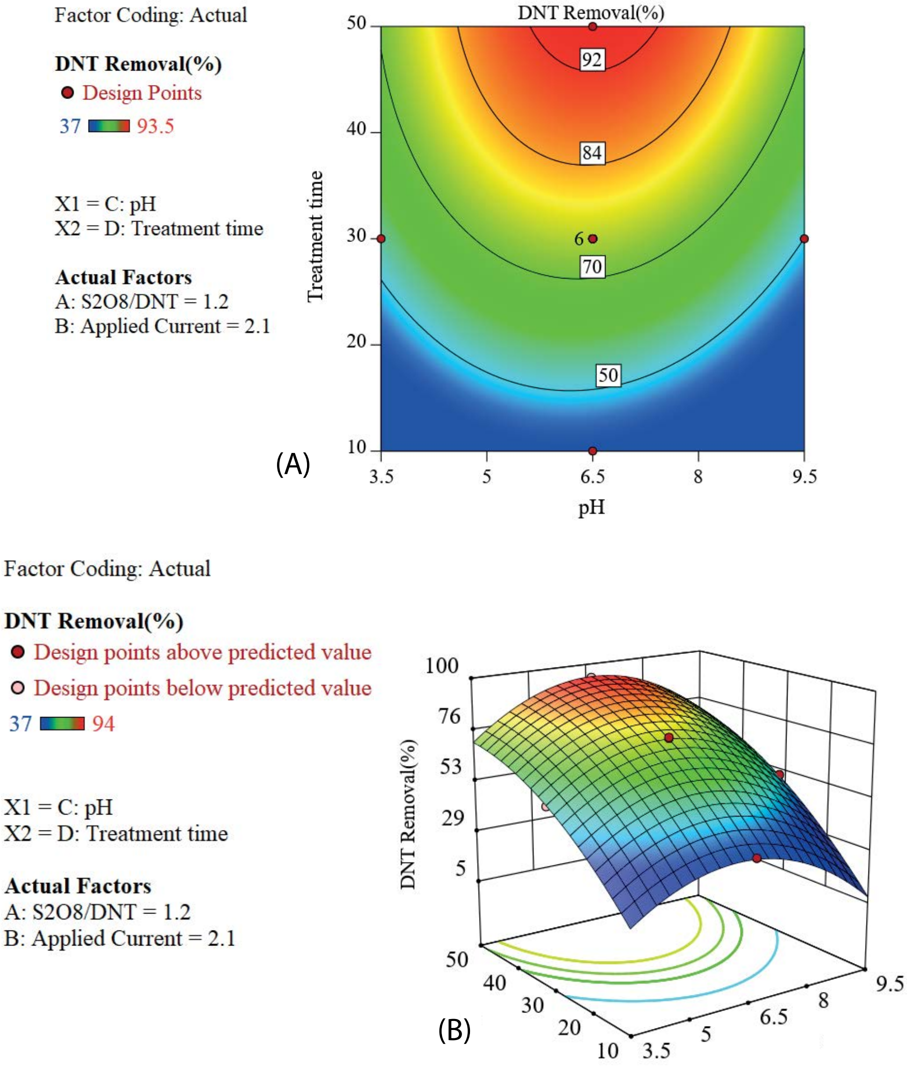

Fig. 3. (A, B) Influence of pH on DNT removal effectiveness at a particular applied current and PDS to DNT ratio.

$$\text{Anode:} \quad Fe \rightarrow Fe^{2+} + 2e^{-} \tag{4}$$

$$\text{Cathode:} \quad 2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(aq)} + 2OH^{-}_{(aq)} \tag{5}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + Fe^{3+} \tag{6}$$

As demonstrated in Eqs. (6)–(8), activation of peroxydisulfate through Fe^{2+} can cause the generation of sulfate radicals. Also, hydroxyl radicals can be produced from sulfate radicals thru the subsequent reactions [Eqs. (6)–(8)]:

$$SO_4^{\bullet -} + H_2O_{(l)} \rightarrow H^{+} + SO_4^{2-} + OH^{\bullet} \tag{7}$$

$$SO_4^{\bullet -} + OH^{-} \rightarrow SO_4^{2-} + OH^{\bullet} \tag{8}$$

Through Fig. 2A and B it is clear that an increase in the peroxydisulfate to DNT ratio can enhance the degradation of DNT to a specific limit and, after that, the rise in the PDS quantity reduces the removal efficacies. Improving the ratio raises the opportunity of producing more sulfate radicals; but, as the amount of sulfate radicals ranges high values, the surplus sulfate radicals, instead of reacting with pollutant molecules, react with each other in the solution, and PDS were formed again [35] [Eqs. (9) and (10)].

Subsequently, the removal efficiency of the pollutant was reduced because the PDS is a weaker oxidant than sulfate radicals. Comparable findings were achieved by Jaafarzadeh et al. [36]. In addition, an extreme increase in the concentration of oxidizing agent above an optimal level to the scavenging of sulfate radicals by $S_2O_8^{2-}$, subsequently dropping the process efficacy [Eqs. (9) and (10)] [37].

$$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-} \tag{9}$$

$$SO_4^{\bullet -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet -} \tag{10}$$

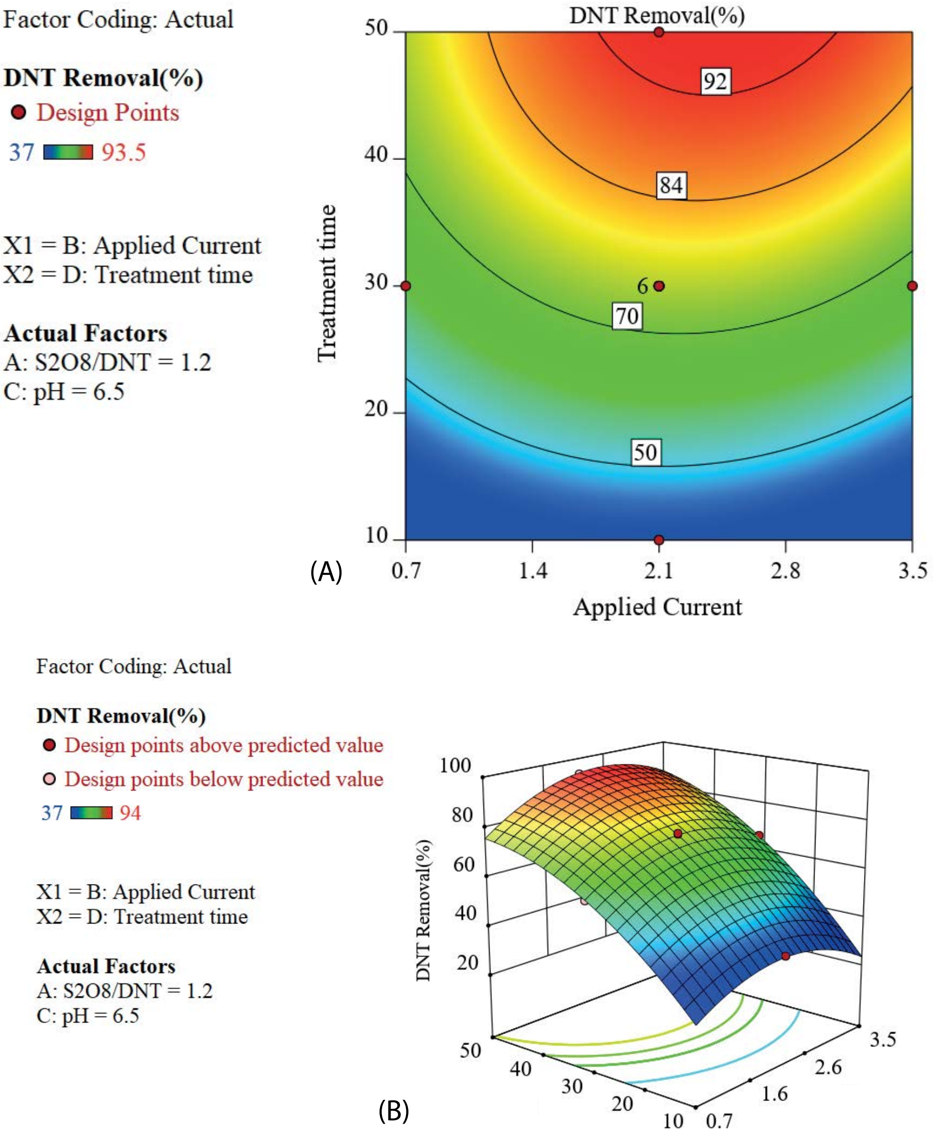

Fig. 4. (A, B) Influence of applied current on DNT removal effectiveness at particular pH and PDS to DNT ratio.

3.4. Influence of pH

Fig. 3 shows the influence of pH at the scope varying from 3.5–9.5 on the DNT removal. Increasing the pH initially forces the DNT removal percent to the greater quantities until the highest value at neutral condition is obtained, and after that additional increase in the pH value has the inverse effect; that is, the DNT removal effectiveness is reduced. It appears that the significant generation of total radicals at the pH value of 6.5 is the main reason for reaching the highest amount of DNT removal value. Its elimination effectiveness was improved because of maintaining greater amounts of radicals that are utilized to degrade the refractory organic constituents. Almost in entire of advanced oxidation processes because of the production of more OH^- and accordingly, more $OH^\bullet$, the scavenging effect of $OH^\bullet$ happened at high pH [38] and relatively low values of pH may influence $SO_4^{-\bullet}$ and $OH^\bullet$. Hence, according to Eqs. 11 and 12, the radicals react with H^+ and result in scavenging influence.

$$H^+ + e^- + OH^\bullet \rightarrow H_2O \tag{11}$$

$$H^+ + e^- + SO_4^{\bullet -} \rightarrow HSO_4^- \tag{12}$$

Furthermore, as shown in Eq. (13), the generated $SO_4^{-\bullet}$ from PDS activation can interact with H^+ in an alkaline environment to produce $OH^\bullet$. Nevertheless, radical scavenging can occur at the additional rise in $OH^\bullet$, and as a result, the degradation of DNT is reduced. Also, as shown in Eq. (14), the $SO_4^{-\bullet}$ can interact with water molecules generating $OH^\bullet$ at pH value 7, while the number of $OH^\bullet$ appears not to be in additional quantities; hence radical scavenging influences cannot occur. As a result, the optimal pH value was obtained at neutral pH, which is in good agreement with the prior research outcomes [39].

Table 3
ANOVA results of response surface model used for DNT removal by EPD process

Source	Sum of squares	DF	Mean square	*F*-value	*p*-value	
Model	6,722.24	12	560.19	1,399.69	<0.0001	Significant
A: S_2O_8/DNT	510.60	1	510.60	1,275.81	<0.0001	
B: applied current	39.78	1	39.78	99.40	<0.0001	
C: pH	45.10	1	45.10	112.69	<0.0001	
D: treatment time	4,968.00	1	4,968.00	12,413.16	<0.0001	
AB	5.41	1	5.41	13.51	0.0019	
AC	5.64	1	5.64	14.09	0.0016	
BD	10.08	1	10.08	25.19	0.0001	
CD	9.15	1	9.15	22.86	0.0002	
A^2	82.90	1	82.90	207.14	<0.0001	
B^2	265.90	1	265.90	664.37	<0.0001	
C^2	911.13	1	911.13	2,276.58	<0.0001	
D^2	187.35	1	187.35	468.13	<0.0001	
Residual	6.80	17	0.4002			
Lack of fit	3.70	12	0.3080	0.4954	0.8521	Not significant
Pure error	3.11	5	0.6217			
Cor. total	6729.04	29				

R^2 = 0.999; Adjusted R^2 = 0.998; Predicted R^2 = 0.997; Adeq. Precision = 138.19; C.V.% = 0.971.

$$SO_4^{\bullet -} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \quad (13)$$

$$H_2O + SO_4^{\bullet -} \rightarrow SO_4^{2-} + H^+ + OH^{\bullet} \quad (14)$$

The complex of $(Fe(II)(H_2O))^{2+}$ was generated in an acidic environment; hence the availability of free Fe^{2+} in the mixture was reduced. Following that, the effectiveness of peroxydisulfate and ferrous iron in the removal of DNT was reduced. After adding the peroxydisulfate, the solution pH was significantly reduced, which is because of the presence of acidic $NaHSO_4$ in PDS salt [40]. As a result, in this investigation, the initial pH was set after adding peroxydisulfate.

3.5. Influence of applied current

In the electrochemical processes, the amount of applied current is one of the essential parameters which have a remarkable influence on the degradation effects of various types of pollutants. Changing in applied current can directly influence the electrode potential and the electrochemical reaction of the total surface of the electrode [41]. As illustrated in Fig. 4A and B, the removal rate of DNT was enhanced with an increase in applied current from 0.7 to 2.4 A, which was conducive to generate $SO_4^{-\bullet}$ over the reaction of PDS to produce more $SO_4^{-\bullet}$ through Eq. (6). Adequate current can increase the production of Ferrous ions, which can activate PDS to produce sulfate and hydroxyl radicals, follow-on an increase in the removal of DNT.

In other words, due to Faraday's law, the generations of metal ions on the surface of an anode will increase if the amounts of applied current increase. In this way, increasing the applied current will increase the ratio of iron ions, resulting in further activation of PDS, hence improving the generations of strong $SO_4^{\bullet -}$ radicals. As a result, the degradation of DNT will be increased.

Due to the Faraday principle, the activation of peroxydisulfate is affected directly by the time [42], and the removal efficiency was increased with increasing time. The total process cost is directly influenced by the rise in PDS to DNT ratio, electrical current, and time. According to the findings of other researchers, the increase in electrical current enhances the energy costs [34,43], whereas the raises in PDS to DNT ratio raises the chemical cost.

3.6. Pareto charts

The RSM is an effective statistical-based method to consider the simultaneous effects of some parameters and therefore search for the optimal conditions for desired responses. The important variables that impact the response can be identified through the Pareto chart analysis. The impacts of experimental parameters on responses at optimized conditions in three-dimensional response surfaces and contour plots (Figs. 2–4) were visualized thru Pareto charts (Fig. 5), and the variables were determined, seeing the significant effects at 95% confidence and both of the main effects and their interactions are presented.

The graphical Pareto study is executed to display the influence of each operational variable on the response and analyzed by the following equation [Eq. (15)].

$$P_i = \left(\frac{b_i^2}{\sum b_i^2} \right) \times 100 \quad (15)$$

The term b_i denotes the influence of the numerical coefficient for each variable. The treatment time and the ratio of peroxydisulfate to DNT were the important factors affecting

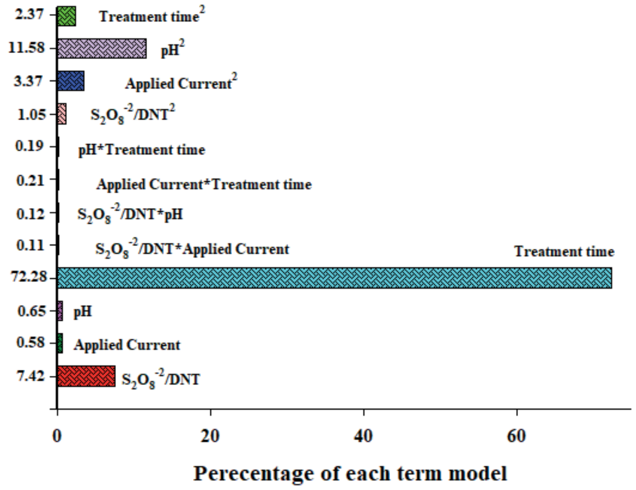

Fig. 5. Pareto chart for the variables in DNT removal.

the removal of DNT. The impact of the applied current and pH was insignificant in the process of the residual contributions. Other researchers achieved similar results using the Pareto chart [44].

3.7. Optimization of operative conditions

The DNT removal efficiency was high at specific conditions, and the amounts of various parameters were optimized by design expert software. The amounts of various factors to maximize the DNT removal are shown in Table 4.

The optimum circumstances predicted by the CCD were as follows: applied current at 2.4 A, pH at 6.5, the ratio of peroxydisulfate to DNT at 1.6, and 40 min of treatment time. The test was repeated at the predicted optimum conditions, and DNT removal was 92.5%. At achieved optimum conditions, about 67% of initial COD was removed, and the amounts of COD were decreased from 350 to 100 mg L^{-1}. The DNT was degraded considerably, but the produced intermediates had COD.

3.8. Electrical energy consumption and cost evaluation

The electrical energy consumed during the process is one of the most important factors in every electrochemical method, as it can impact the economy of the whole process greatly. The consumed electrical energy consumption was calculated at 4.5 kWh kg^{-1} COD removed, using the following equation [45]:

$$\text{EEC}=\frac{U\times I\times t}{V\times\left(Y\times \text{COD}_{\text{initial}}\right)} \tag{16}$$

where I, U, V, t, and Y parameters are applied current (A), cell voltage (V), wastewater volume (L), reaction time (h), and COD removal efficacy (%), respectively.

The electrical energy consumption was estimated to assess the economic possibility of the present study compared to other methods [46]. Due to the following equation [Eq. (17)], the operational cost was estimated.

Table 4
Optimum conditions in the removal of DN.

Parameters	Value
Applied current, *A*	2.4
pH	6.5
$S_2O_8^{-2}$/DNT	1.6
Treatment time, min	40
Predicted DNT removal, %	90.9
Experimental DNT removal, %	92.5

$$\text{Operation Cost}=a\left(C_e\right)+b\left(\text{EEC}\right) \tag{17}$$

where C_e is kg PDS lost and the parameters of b and a are the costs of USD kWh^{-1} and USD kg^{-1} PDS, respectively.

Concerning this fact, the E-PDS method with a lowest EEC and pretty satisfactory removal outcome can be a good choice, when considering the economic and technical aspects of the process concurrently. Therefore, the cost of the process was 0.37 USD kg^{-1} COD removed.

4. Conclusions

The peroxydisulfate activated by iron electrodes was used as an oxidative agent to investigate the removal of DNT from synthetic wastewater. The influence of influential factors, including applied current, the ratio of peroxydisulfate to DNT, pH, and also the treatment time on the DNT removal, was explored. The three-dimensional and contour plots were utilized to analyze the experimental outcomes. The removal of DNT was improved with an increase in the ratio of PDS to DNT. But the influence of pH on the DNT removal effectiveness was not remarkable, and also it has a bit opposite effect in different conditions.

The Pareto chart showed that the treatment time and the ratio of peroxydisulfate to DNT significantly influence the response. The DNT removal efficiency was high at specific conditions, and the amounts of various parameters were optimized by design expert software. The optimal situation was achieved as pH at 6.5, $S_2O_8^{-2}$/DNT = 1.6, applied current at 2.4 A, and 40 min of reaction time, in which about 90.9% of DNT was removed at these conditions. At achieved optimum conditions, about 67% of initial COD was removed, and the amounts of COD were decreased from 350 to 100 mg L^{-1}. The DNT was degraded considerably, but the produced intermediates had COD. In the reached optimum circumstances, the EEC and cost evaluation for E-PDS were achieved at 4.5 kWh kg^{-1} COD removed and 0.37 USD kg^{-1} COD removed, respectively.

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